

# Synthesis and structure of the (tetrahydroxy)oligosiloxane [(<sup>t</sup>BuO)<sub>3</sub>SiOSi(OH)<sub>2</sub>]<sub>2</sub>O

Ron Rulkens, Martyn P. Coles and T. Don Tilley\*

Department of Chemistry, University of California Berkeley, Berkeley, CA 94720-1460, USA  
Chemical Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road,  
Berkeley, CA 94720, USA

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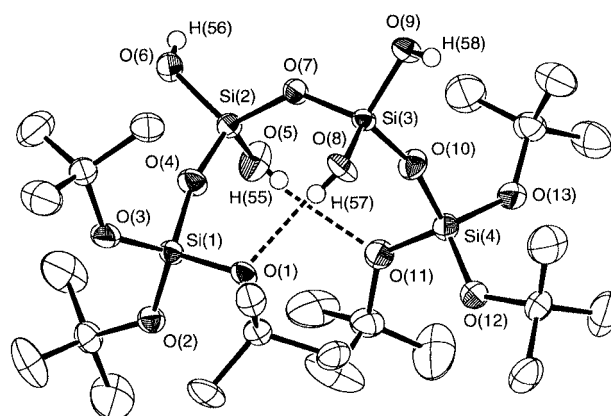
The solid-state structure of the (tetrahydroxy)oligosiloxane [(<sup>t</sup>BuO)<sub>3</sub>SiOSi(OH)<sub>2</sub>]<sub>2</sub>O, synthesized by the hydrolysis of (<sup>t</sup>BuO)<sub>3</sub>SiOSiCl<sub>3</sub>, reveals molecules composed of four vertex-linked SiO<sub>4</sub> tetrahedra and containing four SiOH groups involved in both intermolecular and intramolecular hydrogen-bonding.

Silanol compounds serve as interesting models for the surface hydroxyl groups of silica, and are useful in the synthesis of metal siloxy derivatives containing Si–O–M linkages.<sup>1–4</sup> However, as the number of hydroxyl functionalities per silicon atom increases, these compounds become more unstable toward condensation reactions, hampering the application of silanediols (R<sub>2</sub>Si(OH)<sub>2</sub>) and silanetriols (RSi(OH)<sub>3</sub>) in molecular chemistry. Silanetriols are particularly susceptible to polycondensation in solution to afford *closo*-silsesquioxane species such as R<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>.<sup>5</sup> The judicious choice of R groups, and modifications of synthetic procedures, allow isolation of the incompletely condensed silsesquioxanes R<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub>,<sup>6</sup> which have been used as ligands in main-group and transition-metal complexes.<sup>2</sup> In addition, sterically demanding groups on silicon have allowed isolation of a number of silanediols, silanetriols and disiloxanediols.<sup>1–4</sup> Cyclic structures containing multiple Si–OH functionalities include compounds of the type [ArN(SiMe<sub>3</sub>)Si(OH)O]<sub>3</sub><sup>7</sup> and *cis-cis-cis*[(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Si<sub>4</sub>O<sub>4</sub>(OH)<sub>4</sub>].<sup>8</sup>

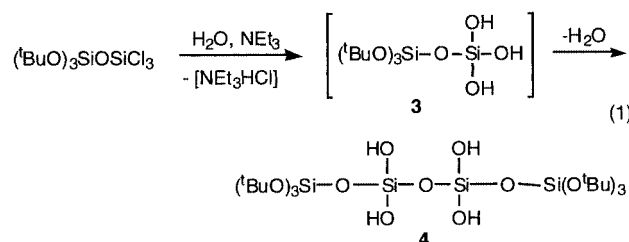
We are interested in the design and synthesis of oxygen-rich metallasiloxane derivatives that undergo facile, low temperature pyrolyses to homogeneous (atomically well-mixed) metal–silica materials, and have previously shown that tris(*tert*-butoxy)silanol, HO-Si(O<sup>t</sup>Bu)<sub>3</sub> (1), and bis(*tert*-butoxy)silanediol, (HO)<sub>2</sub>Si(O<sup>t</sup>Bu)<sub>2</sub> (2), are excellent starting materials for the preparation of suitable metal siloxide precursors.<sup>11</sup> Furthermore, the oxygen environment of the silicon atoms in these molecular species makes them interesting soluble models for heterogeneous, silica-supported catalysts.<sup>11,k</sup> In this communication we describe efforts to synthesize a novel hydroxy-substituted siloxane for use in the synthesis of precursors to silica-based materials. Initial efforts began with attempts to synthesize the reported silanetriol (<sup>t</sup>BuO)<sub>3</sub>SiOSi(OH)<sub>3</sub> (3),<sup>9</sup> which instead resulted in isolation of the (tetrahydroxy)oligosiloxane [(<sup>t</sup>BuO)<sub>3</sub>SiOSi(OH)<sub>2</sub>]<sub>2</sub>O (4). This unusual siloxane is of interest as a model for reactive intermediates in the hydrolytic condensation of tetra(alkoxy)silanes Si(OR)<sub>4</sub> to silica gel.<sup>12</sup>

Attempts to reproduce the literature synthesis of 3 afforded a white crystalline product which exhibits spectroscopic (IR and <sup>1</sup>H, <sup>13</sup>C NMR) and physical (appearance, melting point) characteristics which are very similar to those originally reported.<sup>9,†</sup> To unambiguously determine the structure of the product a single crystal X-ray study was performed, and this revealed the true identity of the product as [(<sup>t</sup>BuO)<sub>3</sub>SiOSi(OH)<sub>2</sub>]<sub>2</sub>O (4).<sup>13</sup> Presumably, 4 forms *via* condensation of the intermediate silanetriol 3 (eqn. (1)).

The infrared spectra of 1, 2 and 4 (KBr pellet) contain Si–OH vibrations in the range 3200–3500 cm<sup>–1</sup>, indicating the presence of hydrogen bonding within the molecules.<sup>1</sup> These

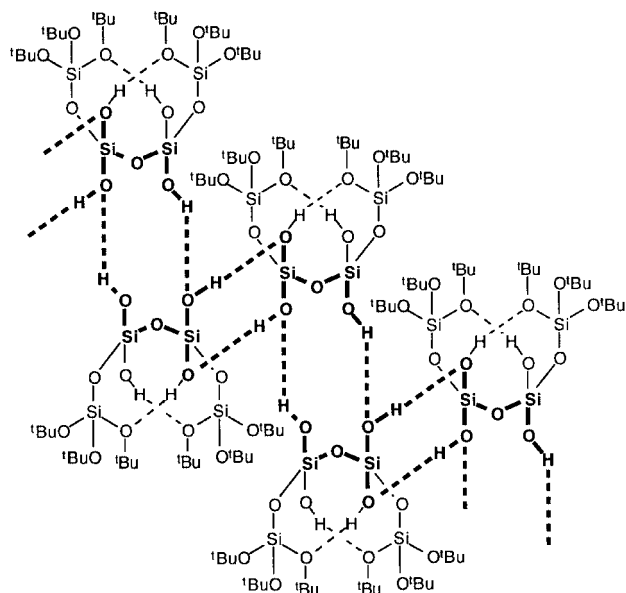


**Fig. 1** Structure of 4: hydrogen atoms of the <sup>t</sup>Bu groups are omitted for clarity; dashed lines represent hydrogen bonds. Selected distances (Å) and angles (°): O(1)⋯H(57) = 2.02(3), O(11)⋯H(55) = 2.35(3); Si(2)–O(7)–Si(3) = 137.7(1), Si(1)–O(4)–Si(2) = 165.7(2), Si(3)–O(10)–Si(4) = 163.6(2).



values are shifted from those for silanol functionalities of dehydrated silica, which exhibit bands at *ca.* 3750 ± 10 cm<sup>–1</sup> (ν<sub>OH</sub>) and 770–840 cm<sup>–1</sup> (δ<sub>OH</sub>).<sup>14</sup> The broad nature of the ν(OH) band in 3 results from the presence of a number of hydrogen-bonding interactions, as revealed in the solid state structure (*vide infra*). The presence of a Si–O–Si group in 4 results in a Si–O vibration at 1138 cm<sup>–1</sup>. The <sup>29</sup>Si NMR spectrum of 4 (CDCl<sub>3</sub>) contains a sharp peak at δ –90.3 for the Si(O<sup>t</sup>Bu)<sub>3</sub> group, and a broad peak at δ –103.2 for the Si(OH)<sub>2</sub> silicon atoms.

The molecular structure of 4<sup>‡</sup> contains two intramolecular hydrogen bonds (H(55)⋯O(11) = 2.35(3) Å; H(57)⋯O(1) = 2.02(3) Å) which appear to distort the silicon–oxygen backbone of the molecule into a parabolic shape (Fig. 1). As a consequence, the central Si(2)–O(7)–Si(3) angle of 137.7(1)° is much smaller than the Si(1)–O(4)–Si(2) and Si(3)–O(10)–Si(4) angles of 165.7(2) and 163.6(2)°, respectively. A similar bending in [Os(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>Si(OH)<sub>2</sub>]<sub>2</sub>O arises from an intramolecular interaction between one SiOH group and a chloride ligand.<sup>15</sup> The compound [ArN(SiMe<sub>3</sub>)Si(OH)<sub>2</sub>]<sub>2</sub>O also adopts a bent structure, which apparently results from association of the molecules in the solid state to form a trimeric cage.<sup>7</sup> The lack of intramolecular interactions in [<sup>t</sup>BuSi(OH)<sub>2</sub>]<sub>2</sub>O<sup>16</sup> and [ArN(SiMe<sub>3</sub>)SiCl<sub>2</sub>]<sub>2</sub>O (Ar = 2,6-<sup>i</sup>PrC<sub>6</sub>H<sub>3</sub>)<sup>7</sup> results in linear Si–O–Si



**Fig. 2** Representation of the intermolecular hydrogen-bonding interactions in **4**, which give rise to the 8- and 12-membered rings shown in bold.

linkages. Also present within the structure of **4** are two sets of intermolecular hydrogen bonds which link the molecules together to form 8- and 12-membered rings, each of which includes an inversion center (Fig. 2). The O(9)–H(58)···O(8) hydrogen bond (2.12(3) Å) supports the 8-membered ring, whereas the O(6)–H(56)···O(9) interaction (1.93(3) Å) is part of the 12-membered ring. Together, these intermolecular hydrogen bonds link the molecules into a chain structure which repeats along the *a*-direction. Multiple intermolecular hydrogen bonds are also present in  $[\text{tBuSi}(\text{OH})_2]_2\text{O}$ , resulting in assembly of the molecules into a sheet-like structure in the solid state.<sup>16</sup>

Compound **4** is relatively stable towards further condensation in the solid state and in solution, but exposure to air for extended periods results in an insoluble material. The thermogravimetric analysis of **4** (heating rate 2 °C min<sup>−1</sup> to 600 °C, 10 °C min<sup>−1</sup> to 1100 °C, oxygen flow) revealed a 50% weight loss between 60 and 140 °C. Further heating resulted in an additional sharp weight loss to 26.9 wt% (between 240 and 290 °C), corresponding to the theoretical yield for 3 SiO<sub>2</sub> (27.0 wt%). These data indicate that **4** may serve as a useful precursor for silica at relatively low temperatures. In contrast, **1** sublimes under similar conditions, so that its use in pyrolytic transformations to silica-based materials is somewhat limited. Preliminary reactivity studies with <sup>n</sup>BuLi, with formation of the siloxide backbone is cleaved by <sup>n</sup>BuLi, with formation of LiOSi(O<sup>t</sup>Bu)<sub>3</sub> as the only isolated product.

In conclusion, the compound previously reported as (tBuO)<sub>3</sub>SiOSi(OH)<sub>3</sub><sup>9</sup> has been reformulated as the condensation product [(tBuO)<sub>3</sub>SiOSi(OH)<sub>2</sub>]<sub>2</sub>O. Further studies will focus on the synthesis of transition metal derivatives of this species.

## Acknowledgements

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## Notes and references

† Selected characterization data for **4**: mp 114–118 °C (lit. value for **3**:<sup>9</sup> 114–117 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.83 (br, OH), 1.33 (O<sup>t</sup>Bu); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 73.10 (CMe<sub>3</sub>), 31.53 (CMe<sub>3</sub>); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ −90.3 (Si(O<sup>t</sup>Bu)<sub>3</sub>), −103.2 (Si(OH)<sub>2</sub>). IR (solid, KBr, cm<sup>−1</sup>) 3438, 3302

(ν(Si–OH), H-bonded), 2977, 2936, 2911, 2874, 1391, 1368, 1245, 1190, 1138, 1066, 998, 876, 829, 700, 507, 484, 436. Anal. Calc. for C<sub>24</sub>H<sub>58</sub>O<sub>13</sub>Si<sub>4</sub>: C, 43.21; H, 8.76. Found C, 43.02; H, 8.59%.

‡ Crystal data: C<sub>24</sub>H<sub>58</sub>O<sub>13</sub>Si<sub>4</sub>, *M* = 667.07, colorless crystals, space group *P* $\bar{1}$ , triclinic, *a* = 9.4952(6), *b* = 14.1078(8), *c* = 15.3210(9) Å, *a* = 112.688(1), *β* = 93.374(1), *γ* = 90.217(1)°, *U* = 1889.5(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.176 g cm<sup>−3</sup>, Mo-Kα radiation, λ = 0.71069 Å, μ = 0.209 mm<sup>−1</sup>, *T* = 156 ± 1 K, *R* = 0.049, *R*<sub>w</sub> = 0.058 for 4741 observed reflections (*I* > 3.00σ(*I*)). CCDC reference number 186/1828. See <http://www.rsc.org/suppdata/dt/b0/b000322k/> for crystallographic files in .cif format.

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